

TITLE OF THE INVENTION

STEEL SHEET WITH LOW ALUMINUM CONTENT FOR CONTAINERS

BACKGROUND OF THE INVENTION

5 Field of the Invention:

The present invention relates to the area of steels for application in the field of metal containers for food, non-food products or industrial purposes.

Discussion of the Background

The steels smelted for uses specific to metal containers differ from thin sheets in particular by their physical characteristics.

The thicknesses of steel sheets for containers vary from 0.12 mm to 0.25 mm for the great majority of uses, but can reach greater thicknesses, as much as 0.49 mm, for very special applications. This is the case, for example, of certain containers for non-food products, such as certain aerosols, or the case of certain industrial containers. Their thickness can also be as small as 0.08 mm, in the case of food receptacles, for example.

Steel sheets for containers are usually coated with a metal coat (tin, which may or may not be remelted, or chrome), on which there is generally deposited an organic coat (varnish, inks, plastic films).

20 In the case of two-piece containers, these are made by deep-drawing under a blank holder or by deep-drawing/trimming for beverage cans, and are generally cylindrical or frustoconical, axially symmetric carts. The container designers are showing increasing interest in even thinner steels, however, with thickness from 0.12 mm to 0.075 mm and, with the objective of distinguishing themselves from the competitors, they are trying to introduce increasingly more complex shapes. Thus we now find cans of original shapes, manufactured
25 from steel sheets of small thicknesses, which sheets, even though presenting greater forming difficulties, must meet the use criteria (mechanical durability of the containers, resistance to the axial load to which they are subjected during storage in stacks, resistance to the internal overpressure to which they are subjected during sterilizing heat treatment and to the internal partial vacuum to which they are subjected after cooling) and therefore must have very high

mechanical strength.

Thus the use and performance of these containers are believed to depend on a certain number of mechanical characteristics of the steel:

- coefficient of planar anisotropy, ΔC aniso,
- Lankford coefficient,
- yield strength R_e ,
- maximum rupture strength R_m ,
- elongation $A\%$,
- distributed elongation $A_g\%$.

To impart to the container equivalent mechanical strength at smaller steel thickness, it is especially preferable that the steel sheet present a higher maximum rupture strength.

It is known that containers can be made by using steels with low aluminum content, and in particular steels known as "renitrided low-aluminum steels". Such a steel is, for example, described in French Patent Application No. 95-11113.

The carbon content usually sought for this type of steel ranges between 0.050% and 0.080%, the manganese content between 0.20% and 0.45%. The aluminum content is controlled to a value of less than 0.020% with the objective of imparting to the steel sheet an improved microstructure, good freedom from inclusions and, consequently, high mechanical characteristics.

The nitrogen content is also controlled, and ranges between 0.008 and 0.016%. This nitrogen content is ensured by addition of calcium cyanamide to the ladle during smelting of the steel, or by blowing gaseous nitrogen into the steel bath. The known benefit of the nitrogen addition is to harden the steel by solid-solution effect.

These steel sheets are made by cold rolling a hot strip to a cold-rolling ratio of between 75% and more than 90%, followed by continuous annealing at a temperature of between 640 and 700°C, and a second cold-rolling with a percentage elongation which varies between 2% and 45% during this second cold-rolling depending on the desired level of maximum rupture strength R_m .

For steels with low aluminum contents, however, high mechanical characteristics are associated with poor elongation capacity. This poor ductility, apart from the fact that it is unfavorable to forming of the container, leads during such forming to thinning of the walls, a phenomenon which will be unfavorable to the performances of the container.

Thus for example, a "renitnded low-aluminum" steel with a maximum rupture strength R_m on the order of 550 MPa will have a percentage elongation $A\%$ on the order of only 2 to 5%.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a steel sheet with low aluminum content for containers, which sheet has a higher percentage elongation $A\%$ than that of conventional steels with low aluminum content but equivalent level of maximum rupture strength.

This and other objects have been attained by the present invention, the first embodiment of which provides a process for manufacturing a steel strip with low aluminum content, which includes:

hot-rolling a steel strip including between 0.050 and 0.080% by weight of carbon, between 0.25 and 0.40% by weight of manganese, less than 0.020% by weight of aluminum, and between 0.010 and 0.014% by weight of nitrogen, the remainder being iron and inevitable trace impurities, to form a strip;

subjecting the strip to a first cold-rolling, to produce a cold-rolled strip;

annealing the cold-rolled strip, to form an annealed cold-rolled strip;

optionally, subjecting the annealed cold-rolled strip to a secondary cold-rolling;

wherein the annealing is a continuous annealing comprising:

raising the temperature of the strip to a temperature higher than the temperature of onset of pearlitic transformation Ac_1 ,

holding the strip above this temperature for a duration of longer than 10 seconds,

rapidly cooling the strip to a temperature below 100°C at a cooling rate in excess of 100°C per second,

thermally treating the strip at a low temperature ranging between 100°C and 300°C for a duration in excess of 10 seconds, and

cooling the strip to room temperature.

Another embodiment of the invention provides a steel strip, produced by the above process.

Another embodiment of the invention provides a steel sheet with low aluminum

content, which includes:

between 0.050 and 0.080% by weight of carbon,

between 0.25 and 0.40% by weight of manganese,

less than 0.020% by weight of aluminum, and

between 0.010 and 0.014% by weight of nitrogen, the remainder being iron and inevitable trace impurities, wherein

when in an aged condition said sheet includes a percentage elongation A% satisfying the relationship:

$$(750 - R_m)/16.5 \leq A\% \leq (850 - R_m)/17.5$$

where R_m is the maximum rupture strength of the steel, expressed in MPa.

Another embodiment of the invention provides a container, which includes or is made from the above-mentioned steel sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

Figs. 1 and 2 are diagrams showing the influence of annealing temperature on maximum rupture strength R_m ;

Fig. 3 is a diagram showing the influence of cooling rate on maximum rupture strength R_m ;

Fig. 4 is a diagram showing the influence of cooling rate on maximum rupture strength R_m and on the percentage elongation A%;

Fig. 5 is a diagram showing the influence of cooling rate on hardness HR30T;

Fig. 6 is a diagram showing the influence of the thermal treatment at low temperature on maximum rupture strength R_m ;

Fig. 7 is a diagram showing the influence of the thermal treatment at low temperature on the percentage elongation A%;

Fig. 8 is a diagram showing the influence of the plastic deformation by elongation on maximum rupture strength R_m .

DETAILED DESCRIPTION OF THE INVENTION

Various other objects, features and attendant advantages of the present invention will be more fully appreciated as the same becomes better understood from the following detailed description of the preferred embodiments of the invention.

5 Preferably, the process for manufacturing a steel strip with low aluminum content for containers includes:

10 - a hot-rolled steel strip is supplied which contains by weight between 0.050 and 0.080% of carbon, between 0.25 and 0.40% of manganese, less than 0.020% of aluminum, and between 0.010 and 0.014% of nitrogen, the remainder being iron and the inevitable trace impurities,

- the strip is passed through a first cold-rolling,
- the cold-rolled strip is subjected to annealing,
- a secondary cold-rolling is performed If necessary, characterized in that the annealing is a continuous annealing in which the cycle includes:
 - a temperature rise up to a temperature higher than the temperature of onset of pearlitic transformation Ac_1 ,
 - holding the strip above this temperature for a duration of longer than 10 seconds,
 - rapidly cooling the strip to a temperature of below 100°C at a cooling rate in excess of 100°C per second.
- a thermal treatment at low temperature ranging between 100°C and 300°C for a duration in excess of 10 seconds,
- and a cooling to room temperature.

According to a preferred embodiment of the process according to the invention:

25 - after rapid cooling of the strip and prior to thermal treatment at low temperature, a plastic deformation operation is performed by elongation of the strip with a percentage elongation ranging between 1 and 5%;

- the strip is maintained during annealing at a temperature of between Ac_1 and 800°C for a duration ranging from 10 seconds to 2 minutes;
- the cooling rate is between 100°C and 500°C per second;
- 30 - the strip is maintained during the thermal treatment at low temperature ranging between 100°C and 300°C for a duration ranging between 10 seconds and 2 minutes;
- the plastic deformation operation by elongation of the strip is performed by

planishing under traction or by rolling.

The invention also preferably relates to a steel sheet with low aluminum including by weight between 0.050 and 0.080% of carbon, between 0.25 and 0.40% of manganese, less than 0.020% of aluminum, and between 0.010 and 0.014% of nitrogen, the remainder being iron and the inevitable trace impurities, which steel is manufactured according to the foregoing process, characterized in that it has in the aged condition a percentage elongation A% satisfying the relationship:

$$(750 - R_m)/16.5 \leq A\% \leq (850 - R_m)/17.5$$

where R_m is the maximum rupture strength of the steel, expressed in MPa.

According to another preferred embodiment of the invention, the steel contains COTTRELL atmospheres and/or epsilon carbides precipitated at low temperature, and it has a grain count per mm^2 greater than 30000.

Influence of the composition of the steel

Preferably, the invention does not relate to the composition of the steel, which is a standard steel with low aluminum content.

As for all renitrided steels with low aluminum content, it is believed that the aluminum and nitrogen contents are important:

- the aluminum is used to kill the steel. It is limited to 0.020% (preferably less than or equal to 0.015%, and more preferably less than or equal to 0.010%) in order to impart to the steel sheet an improved microstructure, good freedom from inclusions and, consequently, high mechanical characteristics;

- the nitrogen content is also controlled, and ranges between 0.008 and 0.016% (preferably between 0.009 and 0.014%, and more preferably between 0.010 and 0.012%).

This nitrogen content is ensured by addition of calcium cyanamide to the ladle during smelting of the steel, or by blowing gaseous nitrogen into the steel bath. The known benefit of the nitrogen addition is to harden the steel by solid-solution effect.

Carbon and manganese are also two elements which it is preferable to control.

- the carbon content preferably sought for this type of steel ranges between 0.050% and 0.080%, more preferably between 0.055 and 0.075%, and most preferably between 0.060 and 0.070%;

- the manganese content preferably ranges between 0.25% and 0.40%, more

preferably between 0.27 and 0.37%, and most preferably between 0.30 and 0.35%.

Influence of the hot-denaturing conditions.

The continuously annealed renitrided steels with low aluminum content are preferably rolled at a temperature above A_{r3} .

The preferable parameter is the coiling temperature, cold coiling between 500 and 650°C being preferred. More preferably, cold coiling between 500 and 620 °C is carried out, more particularly preferably between 520 and 600 °C, and most preferably between 550 and 585 °C. Hot coiling at a temperature above 650°C presents two drawbacks:

- it generates heterogeneities in mechanical characteristics related to the differences between the cooling rates of the core and the extremities of the strip;
- it leads to a risk of abnormal grain growth, which can occur for certain combinations (temperature at end of rolling, coiling temperature) and can constitute a latent defect both in hot sheet and in cold sheet.

Nevertheless, hot coiling may be achieved by using, for example, a selective coiling method, in which the temperature is higher at the extremities of the strip.

Influence of the cold-rolling conditions

By virtue of the small final thicknesses to be achieved, the range of cold reduction ratio preferably extends from 75% to more than 90%, more preferably from 80% to more than 88%, and most preferably from 82% to more than 85%.

The main factors involved in the definition of the cold reduction ratio are preferably the final thickness of the product, which can be influenced by choice of the thickness of the hot product, and also metallurgical considerations.

The metallurgical considerations are based on the influence of the cold reduction ratio on the microstructural condition and, consequently, on the mechanical characteristics after recrystallization and annealing. Thus, an increase in cold reduction ratio leads to a lower recrystallization temperature, to smaller grains and to higher values of R_e and R_m . In particular, the reduction ratio has a very strong influence on the Lankford coefficient.

In the case of requirements applicable to deep-drawing spurs, it is preferable, for example, to optimize the steel grade, especially the carbon content, and the reduction ratio of cold rolling with the hardness or the desired mechanical characteristics in order to obtain a

metal known as "spur-free metal".

Influence of annealing

It is preferable that the annealing temperature be higher than the point of onset of pearlitic transformation Ac_1 (on the order of 720°C for this type of steel). More preferably, the annealing temperature is higher than 750°C , more particularly preferably higher than 780°C , and most preferably higher than 810°C .

Another important characteristic of the invention resides in the cooling rate, which must be greater than 100°C/s . More preferably, the cooling rate is greater than 120°C/s , more particularly preferably, greater than 130°C/s and most preferably greater than 140°C/s .

While the strip is being held at a temperature above Ac_1 there is formed carbon-rich austenite. The rapid cooling of this austenite allows a certain quantity of carbon and nitrogen to be maintained in free state.

It is therefore preferable to perform rapid cooling, between 100 and 500°C/s , at least to a temperature below 100°C . More preferably between 125 and 475°C/s , more particularly preferably between 135 and 450°C/s , and most preferably between 175 and 425°C/s . If the rapid cooling is stopped before 100°C , the atoms of free carbon and nitrogen will be able to combine and the desired effect will not be achieved. Preferably, the rapid cooling is carried out to a temperature below 90°C , more preferably to below 80°C and most preferably to below 70°C . Rapid cooling to room temperature is also preferred.

It is also possible to perform cooling at a rate faster than 500°C/s , but the Applicant has observed that the influence of an increase in cooling rate beyond 500°C/s is not very significant.

This annealing at high temperature with rapid cooling is followed by a thermal treatment at low temperature, which could be called a pseudo-overaging thermal treatment. An important characteristic of this thermal treatment at low temperature resides in the strip holding temperature, which is to range between 100 and 350°C . More preferably the holding temperature ranges between 120 and 340°C , more particularly preferably between 140 and 330°C and most preferably between 150 and 300°C . The rates of temperature increase and of cooling during this thermal treatment at low temperature are of little importance.

The purpose of this thermal treatment at low temperature is to cause the free carbon atoms to precipitate in the form of fine, disperse low-temperature carbides and/or epsilon

carbides. It also makes possible segregation of the free carbon and nitrogen atoms at the dislocations to form COTTRELL atmospheres.

Figs. 1 and 2 show the influence of annealing temperature at constant cooling rate (target rate 100°C/s; actual rate 73 to 102°C/s on Fig. 1; target rate 300°C/s; actual rate 228 to 331°C/s on Fig. 2) on the maximum rupture strength R_m

It is evident from these figures that, for identical percentage elongation in the second rolling, R_m is clearly greater for the steels annealed at 750°C and at 800°C compared with the same steel annealed at 650°C.

Nevertheless, this influence of annealing temperature on maximum rupture strength R_m is not very perceptible when the percentage elongation in the second cold-rolling is less than 3%. It becomes truly significant preferably starting from 5% elongation in the second cold-rolling.

If the temperature is too high (above 800°C), there occurs at least partial precipitation of the nitrogen in the form of aluminum nitrides. This precipitated nitrogen no longer contributes to hardening of the steel, and the resulting effect is lowering of the maximum rupture strength R_m . There are signs of this phenomenon in Fig. 2, where it is noted that, for percentage elongations greater than 10%, the increase in maximum rupture strength R_m between the sample annealed at 750°C and the sample annealed at 800°C becomes smaller.

The time for which the strip is held between A_{c1} and 800°C must be sufficient to return all the carbon corresponding to equilibrium to solution. A holding time of 10 seconds is preferable to ensure this return to solution of the quantity of carbon corresponding to equilibrium for the steels whose carbon content ranges between 0.020 and 0.035%, and a holding time of longer than 2 minutes, although possible, is impractical and costly. Preferably, the holding time ranges from 15 seconds to 1.7 minutes, more preferably from 20 seconds to 1.5 minutes, more particularly preferably from 25 seconds to 1.3 minutes, and most preferably from 30 seconds to one minute.

Figs. 3 and 4 show the influence of cooling rate at constant annealing temperature (750°C) maintained for 20 seconds.

As can be seen in Fig. 3, at 10% elongation in the second cold-rolling, the maximum rupture strength R_m of the steel is equal to about 560 MPa if the cooling rate is equal to 100°C/s, whereas it reaches only 505 MPa if the cooling rate is equal to 50°C/s.

It is therefore possible to obtain a steel with low aluminum content whose value of

Rm is equal to 560 MPa with only 10% elongation in the second cold-rolling if the cooling rate is equal to 100°C/s, whereas a second cold-rolling must be carried out with a percentage elongation of 17% if the cooling rate is only 50°C/s.

By virtue of this smaller percentage elongation in the second cold-rolling step, it is possible to minimize the loss of ductility of the steel. In Fig. 4, for example, it is evident that the steel whose Rm is equal to 560 MPa has a ductility A% equal to 12.5 when the cooling rate is equal to 100°C/s, whereas it is equal to 5.5 when the cooling rate is equal to 50°C/s.

This observation is also valid for the hardness of the steel. As is evident from Fig. 5, for the same percentage elongation in the second cold-rolling, the hardness of the steel increases if the cooling rate is equal to 100°C/s. This increase of the hardness is due to a higher content of free carbon and/or to the presence of fine and disperse precipitates.

As can be seen on Fig. 6, for a steel annealed for 20 seconds at 750°C and cooled with a cooling rate equal to 100°C/s, then cold rolled with a percentage elongation equal to 10%, the maximum rupture strength Rm increases if a thermal treatment at low temperature is performed after annealing at high temperature. Thus, for example, for Steel A, thermal treatment at 150°C makes it possible to increase the Rm value by approximately 50 MPa with a secondary cold-rolling percentage equal to 10% as compared with the same steel not having been subjected to thermal treatment at low temperature and having been subjected to a secondary cold rolling with percentage elongation equal to 18% (Rm = 560 MPa without thermal treatment at low temperature after annealing at high temperature, and Rm = 590 MPa after thermal treatment at 150°C).

It is noted on this Figure that the maximum rupture strength Rm decreases when the temperature of the thermal treatment exceeds 300°C. For example, after thermal treatment at 350°C, the Rm value is equal only to 540 MPa on an average, which represents a decline of 20 MPa as compared with the same steel obtained without thermal treatment at low temperature, with the exception of the difference in percentage elongation during secondary cold rolling. This decrease in Rm with the temperature of the thermal treatment is due to a precipitation of the carbon in the form of cementite.

As is seen on Fig. 7, the thermal treatment at low temperature also makes it possible to increase the percentage elongation A%, which thus rises from 4.8% on the average to 9%, all other things being equal.

Influence of plastic deformation by elongation

It is preferable to increase the hardening phenomenon of the steel by performing, after rapid cooling of the strip and prior to thermal treatment at low temperature, a plastic deformation operation by elongation of the strip with a percentage elongation ranging between 1 and 5%. Preferably, the percentage elongation ranges between 1.5 and 4.5%, more preferably between 1.7 and 4.2%, more particularly preferably between 1.9 and 4.0%, and most preferably between 2.1 and 3.7%.

This plastic deformation creates dislocations on which there will form, during the thermal treatment at low temperature, COTTRELL atmospheres, that is, accumulations of free carbon and nitrogen atoms around the dislocations generated by the plastic deformation, and/or epsilon carbides. Thus, following the thermal treatment at low temperature, the dislocations generated by the deformation of the material will be immobilized or anchored by these COTTRELL atmospheres, which has the effect of hardening of the steel.

As is seen on Fig. 8, at an identical total percentage elongation, the maximum rupture strength R_m of the steel A increases significantly if a small plastic deformation by elongation is performed between annealing at high temperature and thermal treatment at low temperature. For example, it is seen that for a total percentage elongation equal to 15% implemented a single time after thermal treatment at low temperature, the R_m value is equal to 660 MPa. On the other hand, if an intermediate plastic deformation is performed with a percentage elongation equal to 1%, the total percentage elongation remaining equal to 15% (which means that the percentage elongation is decreased during the secondary cold rolling), the R_m value is equal to 672 MPa. It reaches 700 MPa with an intermediation plastic deformation percentage equal to 3%.

This intermediate plastic deformation by elongation may be performed by planishing under traction or by rolling.

The micrographic analyses of the samples revealed that the grain count per mm^2 is larger (greater than 30000). Preferably, the grain count per mm^2 is greater than 35,000, more preferably, greater than 37,000, more particularly preferably, greater than 39,000, and most preferably greater than 40,000.

Thus this manufacturing process makes it possible to obtain a steel with low aluminum content for containers, including by weight between 0.050 and 0.080% of carbon, between 0.25 and 0.40% of manganese, less than 0.020% of aluminum, and between 0.010

and 0.014% of nitrogen, the remainder being iron and the inevitable trace impurities, which steel has in the aged condition a percentage elongation A% satisfying the relationship:

$$(750 - R_m)/16.5 \leq A\% \leq (850 - R_m)/17.5$$

where R_m is the maximum rupture strength of the steel, expressed in Mpa.

EXAMPLES

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

The following tests relate to two cold coils of steel with low aluminum content, whose characteristics are presented in Table 1 hereinafter.

Table 1

	Contents ($10^{-3}\%$)				Hot rolling			Cold rolling	
	C	Mn	Al	N	Rolling end temp. ($^{\circ}\text{C}$)	Upcoiling temp. ($^{\circ}\text{C}$)	Thickness (mm)	Red. ratio (%)	Thickness (mm)
A	59	345	15	10.5	842	598	2.06	91.2	0.18
B	66	309	17	12	841	587	2.00	87	0.28

The coil symbol is shown in the first column; the second through fifth columns indicate the contents in 10^{-3} wt% of the main constituents of importance. The sixth through eighth columns relate to the hot-rolling conditions: In the sixth column there is indicated the temperature at the end of hot rolling; in the seventh column the coiling temperature; in the eighth column the thickness of the hot strip. Finally, columns nine and ten relate to the cold-rolling conditions: in the ninth column there was indicated the percentage reduction achieved by cold rolling and in the tenth column the final thickness of the cold strip.

These two standard strips were subjected to different annealings followed by second cold-rollings, which were also different.

The holding temperatures in annealing varied from 650°C to 800°C, the cooling rates varied from 40°C/s to 400°C/s, the low-temperature annealing temperatures varied from 150 to 350°C and the percentage elongations in the second rolling varied from 1% to 42%, with or without plastic deformation in intermediate elongation.

5 In addition to the micrographic examinations, the characterization of the metal obtained from these different tests included on the one hand performing tension tests on 12.5 x 50 ISO specimens in the rolling direction and in the cross direction, in both the fresh condition and in the aged condition after aging at 200°C for 20 minutes, and on the other hand determining the hardness HR30T, also in both the fresh condition and in the aged
10 condition.

On the basis of these tests it was demonstrated that it is possible considerably to increase the maximum rupture strength R_m for the same steel with low aluminum content and identical percentage elongation in the second cold-rolling, if a continuous annealing according to the conditions of the invention is performed between the two cold-rollings.

In other words, it was demonstrated on the basis of these tests that it is possible considerably to increase the ductility $A\%$ for the same steel with low aluminum content and identical maximum rupture strength R_m if a continuous annealing according to the conditions of the invention is performed between the two cold-rollings, because the same level of R_m is achieved with a smaller percentage elongation during the second rolling. Thus it becomes possible to obtain steel grades with low aluminum content and an R_m level on the order of 380 MPa without necessitating a second rolling step after annealing, other than, perhaps, a light work-hardening operation known as skin pass, in order to suppress the yield-strength plateau present on the metal upon discharge from annealing.

The entire contents of each of the aforementioned patents, references and published
25 application are hereby incorporated by reference, the same as if set forth at length.

Having now fully described this invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

This application is based on French Patent Application No. 9908419, filed July 1,
30 1999, and incorporated herein by reference in its entirety.